

6,6-Dimethylfulvene is thus seen to be an indicator substrate. The first of its kind, it readily differentiates electrophilic from nucleophilic carbene additions. Moreover, the observed regiochemistries of addition are nicely compatible with theoretical expectations. The overall result again demonstrates the power of combined experimental and theoretical analysis of carbenic reactivity.³⁰ We are continuing our studies of indicator substrates.

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(29) Additions of similarly stabilized carbenes (CF₂, CFOH, and C(OH)₂) to ethylene are calculated to have larger overlap at the transition state for CXY^{HO}/alkene^{LU} interaction than for CXY^{LU}/alkene^{HO} interaction.⁶ These findings parallel our interpretation of the CH₃OCCl/1 reaction. A perceptive referee has pointed out that because both interaction terms contribute to the endocyclic addition of CH₃OCCl, FMO theory might actually incorrectly predict this to be the favored mode of reaction, rather than the (observed) exocyclic addition, to which only the nucleophilic interaction can contribute. An extensive analysis of the reaction surface would be needed in order to locate the transition states and accurately evaluate the FMO interaction terms. This is calculationally impossible for systems as complicated as 1 and CH₃OCCl and would probably also stretch the applicability and accuracy of this approach beyond its limits. The transition state obtained in ref 6 for the model ambiphile HOCCF adding to ethylene shows strong carbene interaction with one carbon of the ethylene. Analogously, the very large LUMO coefficient of C₆ of 1 may be the dominant factor in establishing large overlap at C₆ and thus controlling the regioselectivity of the CH₃OCCl addition to 1.

(30) For a prior example, see: Moss, R. A.; Vezza, M.; Guo, W.; Munjal, R. C.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* 1979, 101, 5088.

On the Heat Capacities of Activation for Displacements at Primary and Secondary Carbon Centers in Water

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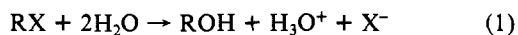
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The heat capacities of activation (ΔC_p^\ddagger) related to solvolytic displacements in water



are invariably negative.¹ An analogy based on other ionogenic reactions in water, e.g., Brønsted acid-base reactions, provides a qualitative explanation for the above observation. Such a model leads to the reasonable conclusion that transition states related to the reactions summarized by eq 1 have considerable ionic character.

Some time ago Albery and Robinson² virtually discarded this model for the case $\text{RX} = \text{tert-butyl chloride}$. These authors postulated that the non-Arrhenius temperature dependence of the solvolytic rates arises as a consequence of an intermediate in the

Table I. Rate and Temperature Data for the Hydrolysis of Ethyl Bromide

| <i>T</i> , °C | <i>k</i> × 10 ⁴ , ^a s ⁻¹ | Δ <i>k</i> × 10 ⁷ , ^b | <i>k</i> (I) × 10 ⁴ , s ⁻¹ | <i>k</i> (II) × 10 ⁴ , s ⁻¹ | <i>k</i> (III) × 10 ⁴ , s ⁻¹ |
|---------------|---|---|--|---|--|
| 90.000 | 6.8313 | 4.04 | 6.8322 | 6.8314 | 6.8298 |
| 85.016 | 4.3503 | 5.13 | 4.3501 | 4.3496 | 4.3612 |
| 80.008 | 2.7252 | 4.82 | 2.7224 | 2.7221 | 2.7310 |
| 80.001 | 2.7230 | 4.08 | 2.7206 | 2.7203 | 2.7291 |
| 74.840 | 1.6493 | 2.08 | 1.6496 | 1.6494 | 1.6527 |
| 69.986 | 1.0117 | 0.58 | 1.0122 | 1.0121 | 1.0122 |
| 65.067 | 0.60518 | 0.56 | 0.60488 | 0.60480 | 0.60418 |
| 62.583 | 0.46255 | 0.46 | 0.46246 | 0.46240 | 0.46203 |
| 57.600 | 0.26463 | 0.26 | 0.26470 | 0.26467 | 0.26545 |

^a The mean of 3-5 determinations, Δ*k* is the standard deviation.

^b The Δ*k* values were used as weighing factors in the Wentworth Regression; Δ*T* was fixed at 0.001 K for all temperatures. The *k*(I) and *k*(II) quantities were calculated from the two sets of values of A, B, C, and D appropriate to eq 7, and *k*(III) was obtained from the values of A, B, and C appropriate to eq 2. The number of significant figures given with respect to *k*, *k*(I), *k*(II), and *k*(III) is that required to calculate Ω to two significant figures.

Table II. Rate and Temperature Data for the Hydrolysis of *sec*-Propyl Methanesulfonate

| <i>T</i> , °C | <i>k</i> × 10 ⁴ , ^a s ⁻¹ | Δ <i>k</i> × 10 ⁷ , ^b | <i>k</i> (I) × 10 ⁴ , s ⁻¹ | <i>k</i> (II) × 10 ⁴ , s ⁻¹ | <i>k</i> (III) × 10 ⁴ , s ⁻¹ |
|---------------|---|---|--|---|--|
| 32.520 | 5.0270 | 1.41 | 5.0251 | 5.0271 | 5.0249 |
| 30.001 | 3.6858 | 3.86 | 3.6889 | 3.6903 | 3.6919 |
| 30.007 | 3.6923 | 4.50 | 3.6916 | 3.6931 | 3.6946 |
| 27.502 | 2.7003 | 1.50 | 2.7011 | 2.7021 | 2.7044 |
| 25.007 | 1.9640 | 1.41 | 1.9640 | 1.9648 | 1.9665 |
| 22.007 | 1.3293 | 1.71 | 1.3291 | 1.3296 | 1.3304 |
| 20.005 | 1.0195 | 1.29 | 1.0189 | 1.0193 | 1.0195 |
| 17.496 | 0.72678 | 1.31 | 0.72570 | 0.72600 | 0.72575 |
| 14.997 | 0.51465 | 0.34 | 0.51389 | 0.51410 | 0.51371 |
| 12.495 | 0.36105 | 0.17 | 0.36102 | 0.36117 | 0.36084 |
| 10.003 | 0.25195 | 0.22 | 0.25199 | 0.25209 | 0.25193 |
| 7.510 | 0.17408 | 0.15 | 0.17440 | 0.17447 | 0.17454 |
| 4.997 | 0.11960 | 0.14 | 0.11928 | 0.11933 | 0.11961 |

^a See footnote a of Table I. ^b See footnote b of Table I.

displacement reaction. Such a postulate is not uncongenial in the case of the tertiary center, but its wider application to primary and secondary substrates was considered to be incorrect.³

A decision between the Albery-Robinson approach and more traditional explanations for non-Arrhenius behavior in displacement reactions is nevertheless difficult, since the magnitude and general behavior of ΔC_p^\ddagger is conditioned largely by the assumptions which underpin its calculation from the rate-temperature (*k*-*T*) data. We recently have shown that the temperature dependence of the rates of hydrolysis of ethyl bromide and *sec*-propyl methanesulfonate demonstrate some features which are in agreement with the Albery-Robinson hypothesis.⁴ This is of considerable interest, since the primary and secondary reactants in question are traditionally considered to be S_N2 or "borderline" substrates. In the present communication we reexamine the temperature dependence of the *k*-*T* data for the two substances mentioned above via the Valentiner equation

$$\ln k = A/T + B \ln T + C \quad (2)$$

which considers ΔC_p^\ddagger to be real rather than anomalous (spurious⁵). Equation 2 also embodies all the "classical" notions concerning the origins of ΔC_p^\ddagger and tacitly assumes that the barrier to activation relates to a single step. In parallel, we also examine the *k*-*T* data for the same substances by using the Albery-Robinson

(3) R. E. Robertson and J. M. W. Scott, *Can. J. Chem.*, **50**, 169 (1972).

(4) M. J. Blandamer, R. E. Robertson, J. M. W. Scott, and A. Vrieling, *J. Am. Chem. Soc.*, **102**, 2585 (1980).

(5) Both "spurious"³ and "anomalous"⁴ have been used to describe that part of the "heat capacity" which is postulated to derive from mechanistic complexity. See also S. Leung and E. Grunwald, *J. Phys. Chem.*, **74**, 687 (1970).

(1) R. E. Robertson, *Prog. Phys. Org. Chem.*, **14**, 203 (1977). For an exception, see J. P. Barron, J. G. Winter, and J. M. W. Scott, *Can. J. Chem.*, **53**, 1051 (1975).

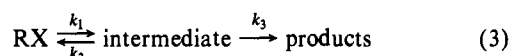
(2) J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, **15**, 980 (1969).

Table III. Derived Temperature-Dependence Parameters^a for the Hydrolysis of Ethyl Bromide and *sec*-Propyl Methanesulfonate

| substrate | eq no. | A | B | C | D | $\Omega \times 10^7$ | $(\Sigma \Delta k^2/n) \times 10^7$ |
|--|--------|---------------------|--------------------|----------------------|---------------------|----------------------|-------------------------------------|
| CH ₃ CH ₂ Br | 2 | -20182.8 ±235.1 | -23.5054 ±0.727 | 186.848 ±4.980 | | 5.87 | |
| | 7 | -18735.5 ±1365.4 | 48.1172 ±4.3594 | -7134.24 ±1280.54 | 23.4374 ±4.1389 | 1.71 | 3.12 |
| | 7 | -11601.3 ±85.8 | 24.6798 ±0.2231 | 7134.24 ±1280.54 | -23.4374 ±4.1389 | 1.88 | |
| (CH ₃) ₂ CHOSO ₃ CH ₃ | 2 | -16214.1 ±163.7 | -16.012 ±0.577 | 137.079 ±3.859 | | 2.70 | |
| | 7 | -15472.7 ±995.9 | 46.1573 ±3.9808 | -4298.91 ±907.11 | 17.1536 ±3.6285 | 1.35 | 1.92 |
| | 7 | -11173.7 ±89.7 | 29.0038 ±0.2650 | 4298.91 ±907.11 | -17.1536 ±3.6285 | 1.71 | |

^a The number of significant figures quoted for A, B, C, and D (eq 7) and A, B, and C (eq 2) is that required to reproduce the reported rate constants to a precision which is comparable to the reported errors of the rate data. The number of digits generally exceeds those justified by the errors from the Wentworth algorithm.

treatment. The main point at issue is whether or not the mechanism



along with the related steady state expression

$$k_{\text{obsd}} = \frac{k_1 k_3}{k_2 + k_3} = \frac{k_1}{1 + \alpha} \quad (4)$$

where $\alpha = k_2/k_3$, will accommodate the k - T data for ethyl bromide and *sec*-propyl methanesulfonate by assuming a simple Arrhenius temperature dependence for the two quantities k_1 and α , such that

$$k_1 = \exp(A/T + B) \quad (5)$$

$$\alpha = \exp(C/T + D) \quad (6)$$

Speculation as to the precise nature of the intermediate in eq 3 is not our concern here; rather, we wish to compare how well the k - T data fit eq 2 with the fit for a combination of eq 4-6, namely,

$$k_{\text{obsd}} = \exp(A/T + B) / [1 + \exp(C/T + D)] \quad (7)$$

Equation 7 requires a nonlinear regression of the k - T data, and the algorithm reported by Wentworth⁶ provides a suitable tool for such an enterprise. The same algorithm can be used for eq 2, although traditionally this calculation has been accomplished by a linear least-squares technique. Since the Wentworth regression is weighted, minor differences related to eq 2 are apparent between the nonlinear and linear calculations, but these are not significant in the present context. Since the Valentiner and Albery-Robinson fits require three and four parameters, respectively, the Gauss criterion for goodness of fit (Ω)

$$\Omega = [\sum \delta^2 / (n - p)]^{1/2} \quad (8)$$

is used to assess the relative merits of eq 7 and 2 where $\delta = k_{\text{obsd}} - k_{\text{calcd}}$, n = number of (k - T) pairs, with $p = 3$ (A, B, and C) for the Valentiner equation and $p = 4$ (A, B, C, and D) for the Albery-Robinson expression.

The data in Tables I and II show the Albery-Robinson equation to be distinctly superior for both substrates. It is of interest to note that the Albery-Robinson equation gives rise to two numerical fits (see Table III). These are mathematically equivalent but chemically different when A, B, C, and D are given physical significance (see also Moore⁷).

The present results lend further support to our previous conclusions based on an alternative treatment of the k - T data for ethyl bromide and *sec*-propyl methanesulfonate.⁴ Again we emphasize that the Albery-Robinson approach assumes real ΔC_p^\ddagger terms to be absent in relation to the k_1 and α quantities. This

assumption is probably incorrect, but modification of eq 5 and 6 to accommodate real heat capacity terms would require a six-parameter nonlinear fit. Since the residuals relating the four-parameter nonlinear fits are already small (see Tables I and II) and are less than the sum of the estimated errors on the experimental k values, it appears pointless to include real ΔC_p^\ddagger terms in eq 5 and 6. Thus the present results are indicative rather than definitive as to the existence of intermediates in these reactions. The evidence presented here should nevertheless prove useful in future mechanistic discussions related to these and numerous other displacement reactions which demonstrate a similar non-Arrhenius temperature dependence.

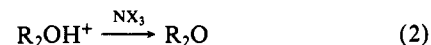
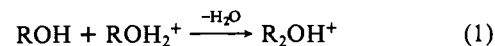
Neutral Products from Nucleophilic Substitution in the Gas Phase. Displacement of Water from Protonated Secondary Alcohols¹

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Many textbooks present second-order nucleophilic substitution as a reaction that exemplifies the use of stereochemical studies to infer transition-state geometry. Inversion of configuration occurs not only in solution but also for anionic S_N2 reactions (displacement of Br⁻ by Cl⁻ on a neutral molecule) in the gas phase.² Recently, Speranza and Angelini³ have described γ -radiolysis studies that suggest backside displacement also predominates in a cationic S_N2 reaction in the gas phase (displacement of HCl by H₂O on protonated methylchlorocyclohexanes). These latter results show only a 2:1 ratio of diastereomers, however, and were run under conditions (e.g., reactants at atmospheric pressure) where the effects of competing pathways and reactions on surfaces are not controlled.



We wish to report the stereochemistry of a cationic S_N2 displacement on a protonated alcohol (reaction 1) under conditions where the effects of competing pathways may be assessed. Over

(6) J. E. Wentworth, *J. Chem. Educ.*, **42**, 96 (1965).

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(8) N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, **66**, 2210 (1970).

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(3) Speranza, M.; Angelini, G. *J. Am. Chem. Soc.* **1980**, *102*, 3115-3120.